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# Materials Selection and Manufacturing of Metal Membranes for Industrial Applications

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## Abstract

In the current scenario, exploration of metal membranes has highly enhanced, and more efforts have been executed in its development and characterization. These breakthroughs have accelerated its applicability in the number of relevant sectors such as waste-water treatments, dairy processing's, wineries, and biofuel refinement. This short letter inspects about recent findings and progress in the field of metal membranes, including its innovative manufacturing techniques and various applications, which have been reported in multiple research papers. The sintering technique is used generally for the preparation of metal membranes. Throughout this process, the resulting pore sizes are in the range of micrometers. Till now it is used for filtration of liquids to separate the solid particles. There is intense research work required for reducing the pore size of metal membranes using some cost-effective novel techniques, which will intensify its applicability in many green filtration technologies.

*Keywords:* Porous materials; Metals and Alloy.

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## 1. Introduction

The performance of the metal membrane is superior to polymeric and ceramic membranes. The beauty of metal membrane lies in its high mechanical

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strength, resistance toward high temperature, ease of sealing and integrated processing. Emerging filtration applications include the separation of higher strength contaminates load or abrasive particulates, which necessitates the applications of porous or dense membranes. Inorganic membranes are prepared by using ceramics and metal powders. It has a higher chemical, mechanical and thermal stability, better filtration features and more extended service life than its counterparts [1]. The presence of such unique properties enhance its application in pharmaceutical, chemical and water purification industries. In metal membranes, these are characterized by a gradient composite structure, consisting of a porous metal base as a substrate and an active separation layer which consists of metal, metal oxides, or metal alloys. When pores get blocked, they can easily be cleaned by high-pressure back flushing [2]. In this letter, we aim to highlight the latest findings on porous metal membranes, their manufacturing techniques, materials and their application in filtration industries.

## 2. Manufacturing Techniques & Materials

In general, porous metal membranes are categorized in two main classes, unsupported metal membranes & porous metal-supported membranes. Thermal sintering is the primary technique for the fabrication of unsupported porous metal membranes [3]. Sintering technique is instrumental in generating smooth and foulant resistant membrane layer, having sharp pore size distributions. This is highly suitable for micro and ultra filtration applications. Size of these pores can be controlled, depending upon their application. The principal benefit of thermal sintering process is that it can manufacture a hollow fibre metal membrane.

As shown in Fig. 1, micro-porous metal membrane, which is fabricated from rolling process. The mean pore size achieved is  $0.7\ \mu\text{m}$ . Thus the resulting removal efficiency of the suspended solids and turbidity showed very slight increment compared to that of an unrolled mesh membrane [4]. Porous SS hollow fibers were manufactured by using micron-sized SS particles. A three-channel

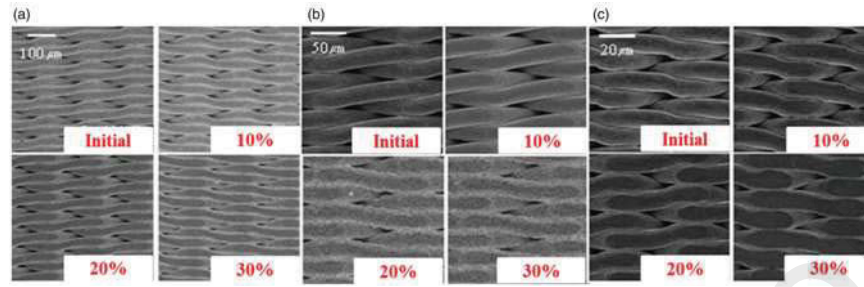


Figure 1: SEM images of new pores as a function of the reduction ratio of a metal mesh using the rolling process [4].

precursor hollow fibers phase inversion techniques were developed using SS powder, which provides better filtration efficiency [5].

Effect of sintering atmosphere air, CO<sub>2</sub>, N<sub>2</sub>, He and H<sub>2</sub> on the microstructure of porous SS hollow fiber is shown in Fig. 2. Porous fibers sintered in Ar atmosphere have a lower flexural strain. Recycled SS316L powders having particle size of 50  $\mu\text{m}$ , is used for making porous metal parts [6, 7].

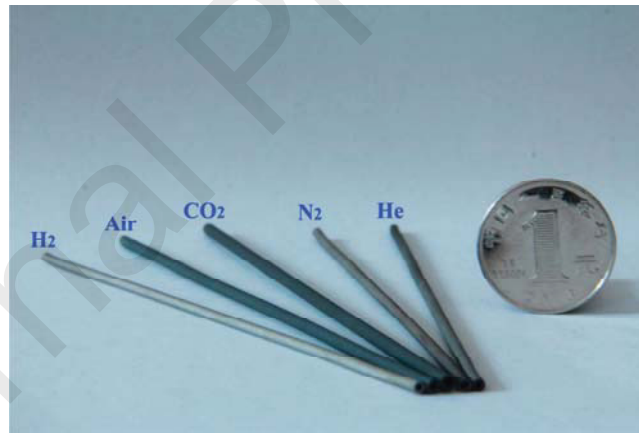


Figure 2: The photo of SS hollow fibre membranes sintered in different atmospheres [8].

Dip coating is used for coating of nano-particles TiO<sub>2</sub> and PVA suspension, on inner surface of tubular membrane. The average size of oil droplet size is 8 $\mu\text{m}$  and resulting average pore size is 0.29  $\mu\text{m}$ . This membrane has a promising potential for the separation of oil/water emulsion [9]. EPD and dip coating techniques applied for manufacturing of novel TiO<sub>2</sub>/Ti-Al composite membranes. The composite membrane has pore sizes in the range of 0.28  $\mu\text{m}$

and a thickness of 40  $\mu\text{m}$  [10]. Ti-Al based metal membranes have shown improved workability and ductility, which is further enhanced by an addition of alloying elements such as Cr, Nb, V, Ta, Si etc. Cold gas spraying is one of the recent developing technology.  $\text{Ti}_{48}\text{Al}_6\text{Nb}$  composite membrane is developed by using the CGS technique followed by reactive sintering at a controlled atmosphere. The resulting pore size is in the range of 1.8  $\mu\text{m}$ . Ti-Al-C porous alloy membranes have attracted the attention of many researchers worldwide. Ternary carbide such as  $\text{Ti}_3\text{AlC}_2$ ,  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{AlC}$  are well known. First, two phases are supposed to be the thermodynamically most stable material. It possesses properties of both metals and ceramics.  $\text{Ti}_3\text{SiC}_2$  is most investigated phase in Ti-Si-C alloys, which works as a potential high-temperature material, in a harsh environment. It is characterized by typical laminate crystal structure and micro-structure [11]. Porous Fe-Al alloys membranes demonstrate excellent oxidation resistance than other metal membranes, such as Ti, Ni and SS 316L. Its peculiar long-range ordered micro structure enhances its resistance towards corrosion, sulfuration resistance at higher temperature [12]. We cannot directly get pore in the range of nano-meter using metal powders, as manufacturing of metal nano powders have not been explored till date.

As shown in Fig. 3, metal anodization techniques are broadly used for surface treatment to render valve materials (Ti & Al etc) with resistance against uncontrolled oxidation, abrasion and corrosion, high strength and hardness values. This technique is relatively inexpensive than sintering. Pore size obtained in this is nearly 40-60 nm. Metal supported, porous anodized aluminium oxide membranes are highly economic for membrane filtration. As it has nano-pores on the top layer, and better chemical and mechanical properties of  $\text{Al}_2\text{O}_3$ . Membrane manufactured by this techniques is brittle and very thin. It should be carefully handled during lab experiment.

### 3. Applications of Metal Membranes

Porous metal filtration process is A green technology, which should be used for sustainable development of any nation. Filtration using metal membranes

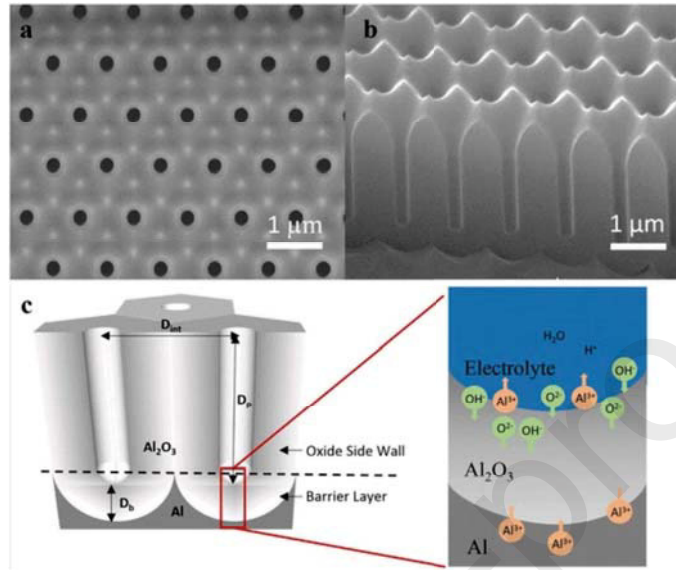


Figure 3: SEM images of imprinted AAO and schematic of AAO structure. a) Top-view. b) Cross-sectional of imprint. c) AAO nanoporous structure and major features of AAO formation [13].

has been studied in various applications such as drinking water treatment, using MF metal membranes with coagulation, rainwater purification using metal membrane and ozonization process. MF metal membrane integrated with electrodialysis for wastewater reclamation and purification of wastewater from industries using (0.2  $\mu\text{m}$ ) Ti metal membrane system. These membranes are capable of removing fat and cod from wastewater, as pretreatment for membrane distillation. Metal Membrane evaporation has emerged as a recent potential technology in this process an aqueous solution is concentrated by a continues evaporation through a porous and heat-conducting membrane. Applications of metal membrane have been recently explored for use as membrane contractors for membrane evaporation processes, which lead to a significant reduction in energy savings. Porous SS membranes (pore size 0.2  $\mu\text{m}$ ) are used in an aerated and submerged bioreactor for the treatment of synthetic domestic sewage, food processing, as they have a excellent stability during steam sterilization [14]. Anaerobic bioreactor and an anoxic/aerobic membrane bioreactor is used for the treatment of synthetic domestic sewage using porous SS membrane (pore

size  $0.4\ \mu\text{m}$ ). Removal of organic impurities in wastewater has been performed by using Photocatalytic metal membranes. Study of denitrification (hydrogenation of nitrate) has been performed by using catalytic metal membrane which consists Pd and Cu metals [15], supported Pd catalysts with Cu or Pb have been used for the reduction of nitrates in aqueous solution. Recently testing for the oxidation of aromatic components in water-based and sea water-based synthetic solution is performed using catalytic metal membrane. Ni and Ni-Cu intermetallics hollow fibre membranes are used for electrocatalytic degradation of small organic molecule contaminants from model waste-water effluents (salicylic acid), these novel porous hollow metal fibre membranes performance are superior as they are highly stable and reusable.

#### 4. Conclusions

In this letter, an overview of the fabrication and applications of metal membranes have been explored. Sintering and metal foaming techniques are mainly used for making porous metal membranes. Though these membranes have some unique properties, the field of the metal membrane has been less studied compared to polymeric and ceramic membranes. Its surface gives a varied array of potential chemistries, & it posses excellent prospects through the novel, economic approaches of manufacturing routes such as de-alloying & electroless deposition, anodizing, and micro-arc oxidation. Significant findings can happen if adequate works are focussed on the combination of these domains of research.

#### References

- [1] M. Duke, R. Semiat, D. Zhao, Target areas for nanotechnology development for water treatment and desalination, *Functional Nanostructured Mater, and Membranes for Water Treatment* (2013) 1–6.
- [2] T. Leiknes, H. Myklebust, H. Ødegaard, Metal membranes for drinking water treatment, *Membrane Techn.* 2005 (4) (2005) 6–10.

- [3] R. Orru, R. Licheri, A. M. Locci, A. Cincotti, G. Cao, Consolidation/synthesis of materials by electric current activated/assisted sintering, *Mater. Scie. and Engi.: R: Reports* 63 (4-6) (2009) 127–287.
- [4] J. Park, S.-H. Min, W.-H. Lee, N.-S. Park, H.-S. Kim, J.-O. Kim, Properties and filtration performance of microporous metal membranes fabricated by rolling process, *Jour. of Water Reuse and Desali.* 7 (1) (2016) 11–15.
- [5] M. Wang, M.-L. Huang, Y. Cao, X.-H. Ma, Z.-L. Xu, Fabrication, characterization and separation properties of three-channel stainless steel hollow fiber membrane, *Jour. of membrane scie.* 515 (2016) 144–153.
- [6] N. E. Gorji, R. O'Connor, A. Mussatto, M. Snelgrove, P. M. González, D. Brabazon, Recyclability of stainless steel (316L) powder within the additive manufacturing process, *Materialia* 8 (2019) 100489.
- [7] N. E. Gorji, P. Saxena, M. Corfield, A. Clare, J.-P. Rueff, J. Bogan, P. G. González, M. Snelgrove, G. Hughes, R. O'Connor, R. Raghavendra, D. Brabazon, A new method for assessing the utility of powder bed fusion (pbf) feedstock through life, *Mater. Charact.* (2020) 110167.
- [8] W. Rui, C. Zhang, C. Cai, X. Gu, Effects of sintering atmospheres on properties of stainless steel porous hollow fiber membranes, *Jour. of Membrane Scie.* 489 (2015) 90–97.
- [9] Z. Li, Z.-L. Xu, B.-Q. Huang, Y.-X. Li, M. Wang, Three-channel stainless steel hollow fiber membrane with inner layer modified by nano-tio<sub>2</sub> coating method for the separation of oil-in-water emulsions, *Separation and Purification Techn.* 222 (2019) 75–84.
- [10] S. Zhou, Y. Fan, Y. He, N. Xu, Preparation of titania microfiltration membranes supported on porous ti-al alloys, *Jour. of Membrane Scie.* 325 (2) (2008) 546–552.



- [11] X. Liu, Y. Jiang, H. Zhang, L. Yu, J. Kang, Y. He, Porous  $\text{Ti}_3\text{SiC}_2$  fabricated by mixed elemental powders reactive synthesis, *Jour. of the Europ. Cer. Socie.* 35 (4) (2015) 1349–1353.
- [12] F. Dobeš, K. Milička, Estimation of ductility of Fe-Al alloys by means of small punch test, *Intermetal.* 18 (7) (2010) 1357–1359.
- [13] Y. Lin, Q. Lin, X. Liu, Y. Gao, J. He, W. Wang, Z. Fan, A highly controllable electrochemical anodization process to fabricate porous anodic aluminum oxide membranes, *Nanoscale resea. lett.* 10 (1) (2015) 495.
- [14] L. F. Dumée, L. He, B. Lin, F.-M. Ailloux, J.-B. Lemoine, L. Velleman, F. She, M. C. Duke, J. D. Orbell, G. Erskine, et al., The fabrication and surface functionalization of porous metal frameworks—a review, *Jour. of Mater. Chemistry A* 1 (48) (2013) 15185–15206.
- [15] K. Daub, G. Emig, M.-J. Chollier, M. Callant, R. Dittmeyer, Studies on the use of catalytic membranes for reduction of nitrate in drinking water, *Chemi. Eng. Scie.* 54 (10) (1999) 1577–1582.

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